Electrochemical Formation of a Film from Lead in Acetate Media.

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In situ formation of a film with alkyl and lead from $Pb(NO_3)_2$ over carbon paste electrodes(CPE) was electrochemically studied. The experiments were carried out at pH=6.65 using acetate buffer as supporting electrolyte. The potential range chosen for the study was -400 to 1600 mV, as it corresponds to the oxidation processes. In this interval, the reduction of Pb(II) (or the reverse process) does not interfere. The number of cycles run were 60. On the first cycle, there is only one oxidation peak that turns into two peaks after the second cycle. The current increased as the number of cycle. Also, an isopotential point is observed starting on cycle 15 and is lost on cycle 23. The film formed is stable and does not change when the electrode is transferred into a supporting electrolyte solution.

To obtain the IR-ATR spectra the growth of the film over ITO was done in the same potential range as stated above, keeping the number of cycle and pH value constant and using (a) supporting electrolyte and (b) lead in the system. In fact, the potentiodynamic profile as obtained during cyclic voltammetry is similar to that obtained with CPE. Data from National Institute of Standards and Technology (NIST) Standard Reference Database [**1**] were used for the assignment of IR bands. The obtained signals are related in (a) to ethane (1394 cm^{-1} and 981 cm^{-1}), acetate ion (1534 cm^{-1} and 1593 cm^{-1}) and water (3314 cm^{-1}). The ethane presence can be explained by the Kolbe reaction [**2-4**]. In (b) can be observed the water and ethane signals, with less intensity than (a), and the slight shift on acetate signals could be due to the coordination between acetate and metallic ions. Furthermore alkyl signals also appear (2850 cm^{-1} and 2920 cm^{-1}) and alcohol signals (3566 cm^{-1} to 3900 cm^{-1}). It is clear that the presence of $Pb(NO_3)_2$ in the solution changes the reactivity of the methyl radicals and IR spectra put in evidence the formation of other hydrocarbon species; because the stretching C-C band (981 cm^{-1}) practically disappears and the methyl stretching bands (2850 cm^{-1} and 2920 cm^{-1}) become intense and very well defined, in the presence of lead.

The micrographs for the films analyzed in the IR-ATR studies was obtained by SEM. The image obtained of the surface using the Pb(II) solutions, where it can be observed the formation of globular and dendritic clusters (white zones). In this case, the semi-quantitative analysis was performed for the inner cluster zones and also for the outer zones. In both cases the presence of lead was detected, in more proportion into the clusters than outside (39.7% and 5%, respectively). This experiment shows that this film contains lead.

IR-ATR and SEM with X-Ray probe experiments allows to propose the bonding between lead and alkyl species.

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